3. MATERIALS FOR EXHAUST AFTERTREATMENT

A. Materials for Exhaust Aftertreatment

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Objectives

- Develop advanced materials applied for diesel engine aftertreatment systems that will comply with future emission regulations.
- Develop a prototype lean-NO_x (nitrogen oxides) catalyst system to demonstrate >50% NO_x conversion with <5% fuel penalty.
- Evaluate capabilities of commercial and near-commercial NO_x sensor technologies to meet future Environmental Protection Agency (EPA) requirement for on-board NO_x monitoring.
- Develop novel NO_x sensor materials and concepts functioning at low NO_x concentrations (<100 ppm).
- Evaluate filtration properties of various sintered metal media for application in diesel particulate filters (DPFs).

Approach

- Identify a reformer technology to provide desirable reductants for selected lean-NO_x catalyst materials, which will maximize NO_x reduction performance.
- Develop catalyst durability test protocols for sulfur and phosphorus poisoning.
- Develop test protocols and evaluate various prototype NO_x sensor technologies.
- Synthesize perovskite-type materials for NO_x sensor application.
- Develop novel NO_x sensor materials based on semiconductors functionalized with organic sensitizers.
- Use our modified test bench and new test protocols to evaluate the capability of various particulate matter trap materials.
- Identify the critical parameters for soot oxidation in catalyzed particulate filters.

Accomplishments

- Identified a promising reformer technology, "reformer-assisted lean-NO_x catalyst system" to achieve high NO_x conversion.
- Performed steady state engine tests and achieved 44% NO_x conversion with 5.6% fuel penalty.
- Identified the challenges of NO_x sensor application, including poor accuracy at low NO_x concentrations (<200 ppm) and cross-sensitivity to other gas components.
- Among prototype NO_x sensors tested, determined that a mixed-potential NO_x sensor showed better performance at low NO concentration below 100 ppm.
- Fabricated perovskite materials in-house that showed the best sensitivity to NO reported in the literature among electrochemical-type NO_x sensor materials.
- Identified semiconductor materials functionalized with organic sensitizers to show pronounced response to low NO concentrations (10 ppm).
- Found a combination of sintered metal materials that provided competitive filtration efficiency and backpressure with substantially lower volume compared with a conventional wall-flow filter material.
- Developed a test protocol that provides reliable soot loading (amount and type of soot) on cordierite, SiC, and sintered metal DPF samples, as well as regenerative capabilities of cordierite filters.

Future Direction

- Assess sulfur and phosphorus poisoning behavior on the lean-NO_x catalysts.
- Document intellectual properties resulting from the lean-NO_x project and transfer the invention to a strategic partner.
- Study the effect of a "rich" exhaust environment and cross-sensitivity of NH_3, H_2S, H_2 and hydrocarbons on NO_x sensor technologies.
- Perform durability and rapid aging tests to assess the lifetime of the selected NO_x sensors.
- Conduct a fundamental study of NO_x -sensing mechanism using a computational modeling technique.
- Catalyze sintered metal materials and evaluate their DPF regeneration features.
- Investigate the effects of temperature, space velocity, and gas composition on the soot oxidation rates in DPF samples.
- Evaluate particulate-matter regeneration and material durability of various DPF materials.

Introduction

The objective of this effort is to develop and evaluate materials that will be used in aftertreatment systems for diesel engine applications to comply with future government emission regulations. The materials include catalysts for NO_x abatement, filtration media for particulate control, and novel materials to improve NO_x sensing capabilities in the exhaust system. This year's focus is on

- development of a prototype reformer-assisted lean-NO_x catalyst system to improve NO_x reduction (>50%) and to minimize fuel penalty (<5%)
- identification of the critical parameters for soot oxidation in a catalyzed particulate filter
- further evaluation of particulate filtration characteristics of sintered metal materials, evaluation of the current state-of-the-art NO_x sensor technologies
- development of novel NO_x sensor materials to improve sensing capabilities at low NO_x concentrations (<100 ppm)

Approach

Lean NO_x. This effort focused on identifying new lean- NO_x catalyst formulations that effectively utilize selected reductants, including H_2, CO, alkane, oxygenated hydrocarbons, or mixtures of these. The concept of reformer-assisted lean- NO_x catalysis has been assessed with various reformer technologies to identify the right reformer technology that is able to provide the desirable reductants to the catalyst materials. A prototype system consisting of a promising catalyst and a selected reformer was developed to conduct engine tests in order to demonstrate the proof of concept.

NO_x sensor. A commercially available NO_x sensor does not demonstrate adequate sensitivity and selectivity to measure the 0.2 g NO_x/bhp*h level proposed for 2010 and OBDII regulations. The objective of this project is to develop a promising NO_x sensor technology capable of meeting or exceeding EPA's 2010 standard for OBDII monitoring systems for diesel engine exhaust emissions. The approach is aimed at thorough evaluation of commercial or nearly-commercial electrochemical NO_x sensors in order to guide sensor developers to further improvements. The development of novel sensor concepts was pursued as an alternative NO_x sensor technology.

Particulate matter trap. Our modified test bench used to evaluate particulate filter materials includes a diesel fuel burner, a chemical reactor, a bench of Horiba analyzers, and a scanning mobility particle sizer (SMPS). The amount of particulate matter captured is determined using the pressure change across the sample, while the efficiency of the filter is determined using SMPS data. The composition of the exhaust from the burner is measured with the Horiba analyzers. The capability of various particulate matter trap materials, including sintered metals, was evaluated using the bench system. The system can easily be adapted to test other materials, such as cordierite and SiC particulate filters.

Results

Lean NO_x

Lean-NO_x catalyst material. A synergy effect was identified when alumina and zeolite-based materials were combined in a specific order. The combination catalyst significantly improves lean-NO_x performance with a liquid hydrocarbon reductant. (Figure 1) The kinetic parameters and the influence of fuel components on NO_x reduction performance over the selected catalyst were obtained using in-house bench test systems to further understand the efficiency of the catalysts and to provide insight into optimization strategies for a reformer technology.

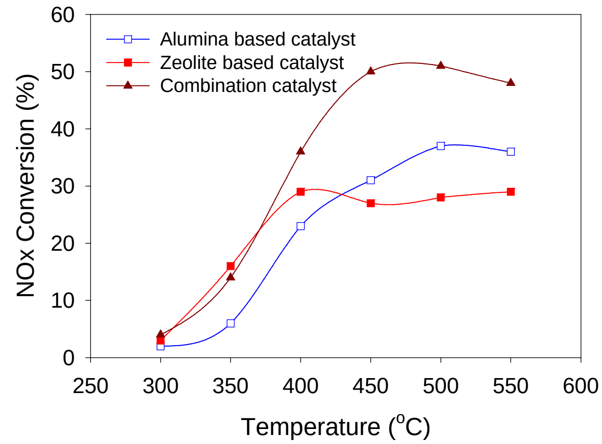

Figure 1. Comparison of NO reduction over individual catalysts and a combination catalyst tested with a liquid hydrocarbon (0.05% NO, C_1/ NO_x =3, 9% O_2, 7% H_2O, 35,000 h^{-1}).

Engine test. The engine tests were performed using two different levels of horsepower (275 and 500 hp) and two different NO_x emission-compliant engines (years 1998 and 2004) with catalysts of two different sizes (17 and 34 L), respectively. The effects of space velocity, catalyst temperature, reductant species, catalyst formulation, and reductant-to-NO_x ratios were studied. The results showed 44% NO_x conversion was achieved with a 5.6% fuel penalty from weighted OICA steady state cycles (nine selected modes). The test results showed that the reformer significantly enhanced NO_x reduction performance and reduced the fuel penalty (Figure 2).

NO_x Sensor

Commercial and nearly-commercial NO_x sensor technologies. Evaluation of state-of-the-art NO_x sensor technology in the presence of 0–1000 ppm ammonia showed that the sensor output increases with increasing NH_3 concentration, while the NO_x analyzer reading (used for control purposes) remained constant (Figure 3). This cross-sensitivity substantially limits sensor applications under "fuel-rich" environments or in the presence of reductants such as NH_3 (ammonia/urea selective catalytic reduction), H_2 (reformer technology), and C_xH_y (hydrocarbons selective catalytic reduction). In addition, the sensor showed poor resolution at low

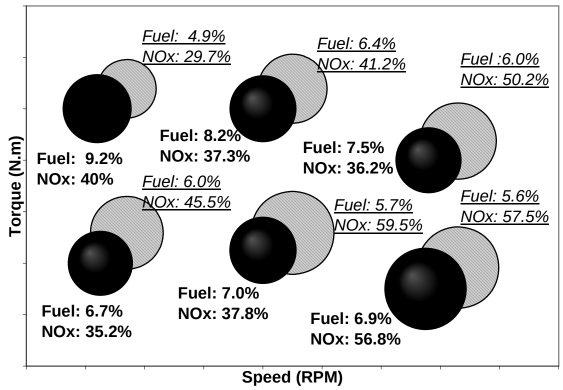

Figure 2. NO_x reduction performance and fuel penalty data obtained from selected OICA steady state cycles of a diesel engine equipped with a prototype reformer-assisted lean- NO_x catalyst system. Black circles: without reformer, Shaded circles: with reformer.

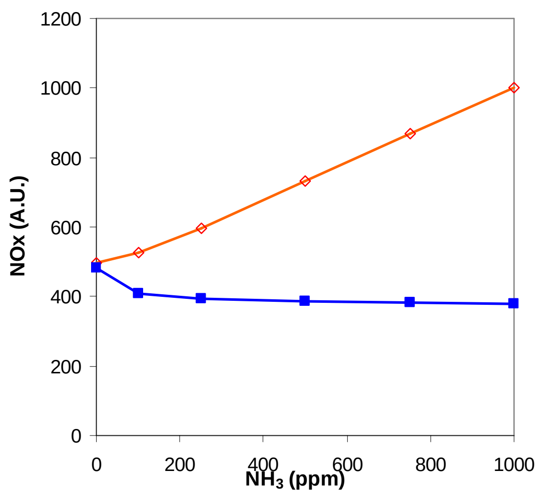

Figure 3. Output from a commercial sensor (diamonds) and a NO_x analyzer (squares) as a function of ammonia concentration.

NO_x concentrations. Evaluation of nearly-commercial NO_x sensor technologies in low NO_x concentrations has been completed. One sensor has been identified as exhibiting a good linear response to low NO concentrations, specifically in the range of 0–20 ppm. Reproducibility tests showed that the sensor response can vary by up to 4.5% and needs further improvement

Perovskite-type NO_x sensor materials. Novel amperometric-type electrodes on yttria-stabilized zirconia (YSZ) as solid electrolyte and La/Fe perovskites (ABO_3 composition) as chemically interactive material (CIM) were prepared in-house by screen-printing and tape-casting techniques (Figure 4). Materials were tested at low NO concentrations (<100 ppm) in the presence of 0–20% O_2 in N_2 at 700–800ºC. Materials exhibited much higher conductivity (up to 400 mA) in comparison with other mixed metal oxides described in the literature and showed better NO_x sensitivity. The CIM cited in literature[1] exhibited an amperometric NO_x sensor output that yielded Δ47 mA for the increment of 500 ppm NO, while the La/Fe materials prepared in our study showed a Δ5–25mA output increase for the increment of 15–50 ppm NO at applied voltages greater than 0.8V (Figure 5). These are the best results reported in the literature for electrochemical type NO_x sensor materials.

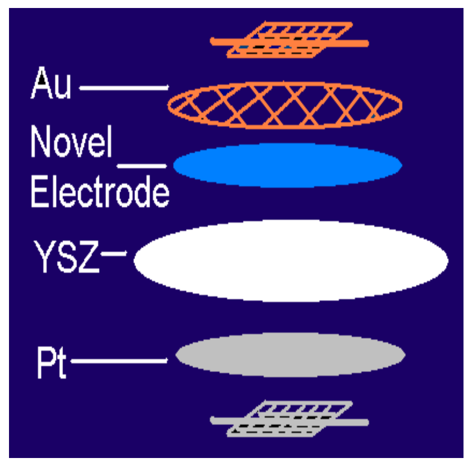

Figure 4. Schematic of a novel electrode fabrication for a NO_x sensor.

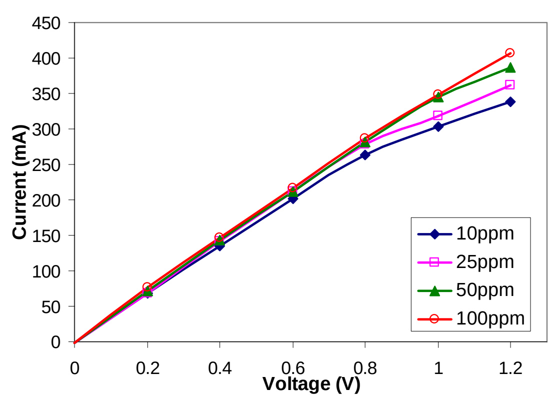

Figure 5. I(V) response curves of an amperometric La/Fe sensor at various NO concentrations (ppm).

Semiconductors functionalized with organic sensitizer NO_x sensor materials. Functionalized semiconductor materials were evaluated for optical detection of NO. Semiconductor-coated quartz substrates were provided by a supplier or prepared in-house by the spray-pyrolysis method using organometallic precursors. The dip-coating method was used to prepare sensitized semiconductor materials. The UV-VIS tests at ambient conditions showed that pronounced response to 10 and 100 ppm NO was exhibited. Therefore, a novel NO_x sensor concept employing functionalized semiconductor materials can be developed. This concept offers many advantages over traditional electrochemical sensor technologies such as direct NO measurement, including no requirement for a catalyst or a heater.

Particulate Matter Trap

We have completed and submitted for publication a work in collaboration with Jinyu Zhu and Kyeong Lee from Argonne National Laboratory on the characterization of particulates produced in our diesel fuel burner, focusing on morphology, microstructures, and fractal geometry. This work revealed that diesel particulate matter produced using the newly developed test protocol shows morphological characteristics similar to those of the particulates produced in diesel engines.

The first and second generations of test protocols were developed for soot oxidation studies on DPFs that provide consistent soot loading on the DPF samples. The protocol was used with our bench to evaluate new DPF filtration media based on sintered metal technology. Preliminary results indicated that a combination of new sintered metal materials yielded competitive filtration efficiency (Figure 6) and backpressure (Figure 7) with substantially lower volume compared with a commercial wall-flow cordierite DPF tested under the same conditions. Further work is in progress to validate the tests described in this report and to apply this approach to regenerate particulate matter accumulated on various filtration materials.

Conclusions

The research has demonstrated a prototype reformer-assisted lean-NO_x system that has the potential to achieve >50% NO_x conversion with a <5% fuel penalty with the optimization of catalyst materials as well as fuel injection strategy. The comercialization plan has been being developed through the collaboration of strategic partners. The current

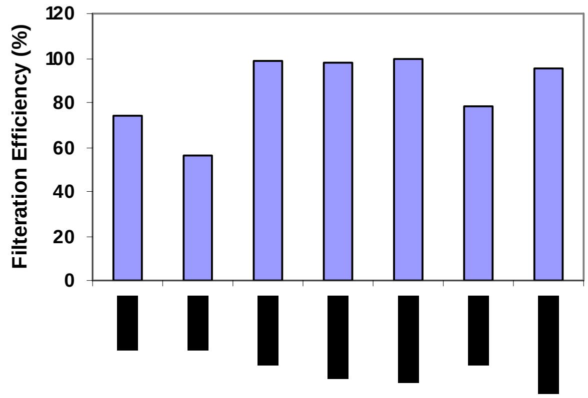

Figure 6. Comparison of filtration efficiencies of various sintered metal media (SM series) and an un-catalyzed wall flow cordierite particulate filter.

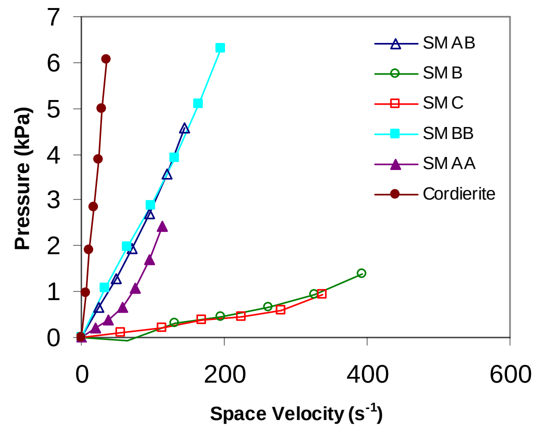

Figure 7. Comparison of backpressure as a function of space velocity for various sintered metal media (SM series) and an un-catalyzed wall flow cordierite particulate filter.

electrochemical NO_x sensor concept has limitations owing to poor accuracy at low NO_x concentrations and cross-sensitivity to ammonia. The novel NO_x sensor concepts studied in this program showed promising results and warrant further development. The testing performed with sintered metal filtration media indicates that this material has competitive filtration efficiency and backpressure compared with a traditional wall-flow cordierite filter and provides a significant reduction in volume. This material, therefore, deserves further testing to confirm these results and examine its regenerative properties.

Reference

1. F. Menil et al., “Critical Review of Nitrogen Monoxide Sensors for Exhaust Gases of Lean Burn Engines,” *Sensors and Actuators B67*, 1–23, 2000.

Publications/Presentations

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Svetlana Zemskova, Paul W. Park, J. S. Lin, J. Wen, and I. Petrov, “Study of High Surface Area Alumina and Ga-alumina Materials for deNO_x Catalyst Applications,” presented at the 28th International Conference and Exposition on Advanced Ceramics and Composites, Cocoa Beach, FL, January 25–30, 2004.

Craig F. Habeger, “Requirements for NO_x Sensors in Heavy Duty Diesel Exhaust Environments,” presented at the 28th International Conference and Exposition on Advanced Ceramics and Composites, Cocoa Beach, FL, January 25–30, 2004.

Jinyu Zhu, Kyeong Lee, Alexander Panov, and Jill Akers, “An Investigation of Particulate Morphology, Microstructures, and Fractal Geometry for a Diesel Engine-Simulating Combustor,” SAE paper 2004-01-3044, Society of Automotive Engineers, 2004.

Patents Issued

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